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Active Sites of Platinized-Platinum Electrodes

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The nature of distribution of the active adsorption centres on the platinized-platinum electrodes has been determined from the anodic galvanostatic charging curves obtained for the oxidation of the adsorbed hydrogen. From the relative aptitude for the adsorption or chemisorption of alcohols, the apparent topography of the crystallites is arrived at.

PLATINIZED-PLATINUM (Pt/Pt) electrodes are preferred to smooth platinum electrodes because of the fact that the number of active reaction sites per geometric (visible) area is many times larger than that in the smooth electrodes. Sometimes there is an enlargement in the number of active sites in some electrolytes. The pattern of distribution of the active reaction centres as a function of temperature in aq. electrolytes and the apparent topography of the deposited crystallites have now been evaluated.

Materials and Methods

The platinization of the electrodes was performed by the low current density (2 mA/cm^2 apparent) deposition procedure described elsewhere[1,2]. After the plating and the pretreatment these electrodes were allowed to age for a few weeks, followed by the accelerated ageing at elevated temperature ($\approx 90°$) for 48 hr[3]. These electrodes took about a week to furnish accurately reproducible equilibrium charging curves in 0·5M H_2SO_4.

The electrolytes and the adsorbates of AR grade were purified with the usual precautions[2]. The anodic galvanostatic charging curves were run at 4°, 60° and 80° and in the desired electrolyte at a hydrogen partial pressure of 1 atm., using the experimental procedure[1,4,5] and the set up[6] described elsewhere. The temperature of the working electrode compartment was accurately controlled ($\pm 0{\cdot}5°$) by circulating preconditioned water in the external jacket of the cell[6]. The preconditioning water in the case of experiments at 4° contained ethylene glycol. All the potentials (φ_r) were measured with a reversible hydrogen electrode (RHE) in the same experimental electrolyte at 25°. Since the working electrode compartment and the reference electrode compartment were at different temperatures, the potential difference caused by the thermal gradient was measured and the necessary correction was applied.

To get some information regarding the topography of the electrodeposit some experiments were performed under open circuit condition and steady state condition of polarization with alcohols. Details of these experiments were described elsewhere[2,4].

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Results and Discussion

From the study made with Pt/Pt electrodes the following results were collected:

(i) The galvanostatic charging curves obtained with freshly plated electrodes showed a very large hydrogen arrest. The true surface area and the roughness factor could be determined from the identity[7] 210×10^{-6} coulomb=1 true cm^2. The roughness factor for fresh eletrodes was found to remain in the range 10^3 to 2×10^3.

(ii) If the fresh electrode was allowed to age at the ambient temperature, then the true surface area was found to decrease and the roughness factor reached a value of about 800 to 1200 and registered almost constant value thereafter.

(iii) If these electrodes were further subjected to ageing at elevated temperatures ($\approx 90°$) then the roughness factor drastically decreased and thereafter remained almost constant in the range 350 to 600.

(iv) If a freshly plated electrode was allowed to come in contact with acid-iodide solution, then the hydrogen arrest decreased. If the iodide adsorbed Pt/Pt electrodes were afterwards used in acid-sulphate solutions, there was initially a partial desorption of the iodide adsorbed resulting in slight gain in the hydrogen arrest.

(v) If the charging curves were run with fresh and aged electrodes in acid-chloride and acid-sulphate media, it was always noticed that the hydrogen arrests were larger by 12% in the case of acid-chloride solutions. An explanation for this was already advanced elsewhere[5,8]. In the present study it will be considered further.

In the present study the behaviour of aged equilibrium electrode was investigated from a somewhat closer microscopic viewpoint. The representative anodic galvanostatic charging curves (Fig. 1) were determined at 4°, 60° and 80° and at 10^{-4} A/cm^2 (geom.). By extrapolating the hydrogen region to zero potential (after applying the correction for thermal potential difference) we have evaluated in each case the period (and hence the charge) required for the oxidation of a complete monolayer of adsorbed atomic hydrogen at the indicated temperatures and the values at 4°, 60° and 80° are 860, 1080 and 1200 sec. For 4 cm^2 visible surface area of the electrode and at a current density of 10^{-4} A/cm^2

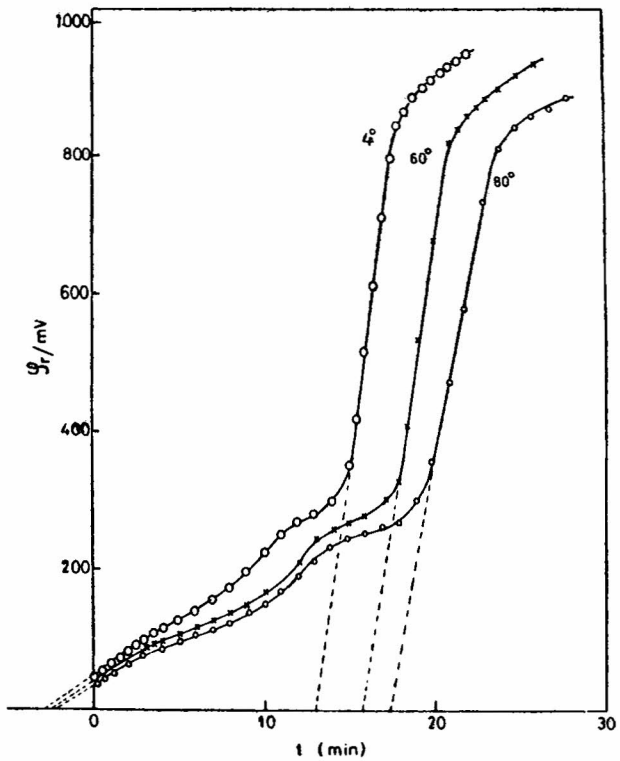

Fig. 1 — Anodic galvanostatic charging curves for the oxidation of hydrogen present on the platinized-platinum electrode at 4°, 60° and 80° and in 0·5M H_2SO_4 at 1×10^{-4} amp/cm² (geom.)

(visible) the charges spent were 0·384, 0·432 and 0·480 coulomb at 4°, 60° and 80° respectively.

The charge spent, Q, increased with increasing temperature and this led to the inference that the population density of the adsorbed atomic hydrogen on the active sites at the monolayer coverage increased with temperature. Hence the Boltzmann distribution for the active sites given by Eq. (1) could be applied to a first approximation.

$$n=n_0 \exp -E_a/RT \qquad ...(1)$$

where n is the number of active platinum sites on which the hydrogen adsorption takes place at the temperature T (°K). E_a is the energy required to activate the site suitable for hydrogen adsorption. From electrodynamics we know that one electron is associated with a charge of $1{\cdot}6021\times10^{-19}$ coulomb. Using this value, the number of electrons (hence the active sites) required for the electro-oxidation of the adsorbed hydrogen was determined. At 4°, 60° and 80° these values work out to $2{\cdot}4\times10^{18}$, $2{\cdot}86\times10^{18}$ and $3{\cdot}0\times10^{18}$ respectively. This increase in the number of electrons with increasing temperature to a first approximation conform to the Boltzmann distribution pattern of energy levels and hence the energy of activation for the excitation of the platinum site could be determined from Eq. (2).

$$\frac{d\ln n}{d1/T}=\frac{d\ln Q}{d1/T}=\frac{-E_a}{R} \qquad ...(2)$$

The experimental activation energy was 573·7 cal per mole. From the values of n and E_a, the value of n_0 was determined for the aged electrode and it remained at $6{\cdot}76\times10^{18}$ sites. On this basis only 44% of the sites are available for the hydrogen adsorption reaction even at 80°. The percentage sites available at 4° and 60° are 35·5 and 42·3 respectively. [In the case of fresh electrodes (just plated ones) the active sites were 3 to 6 times larger than that obtained with aged electrodes. Hence the n_0 value will also be larger by the same factor. The charging curves obtained with very fresh electrodes are not shown here in this paper.]

From the n_0 value we can arrive at the approximate topography of the deposited crystallites present on the electrodes. In the case of aged electrodes 169·5 sites per geometric Å² exist. A single platinum atom itself had been shown[9] to occupy 8·9 Å². Hence about 170 sites per geometric Å² on the 4 cm² of the plated electrode will be plausible only if the crystal growth during plating occurs in the micro-dentritric fashion with many micropores.

It had been observed in a number of instances that the chemisorption of organic substrates on the platinized electrodes occurred on all the sites on which the hydrogen adsorbed. (This was inferred from the fact that the charge required to oxidize the entire monolayer of adsorbed hydrogen layer and the charge required to oxidize the chemisorbed layer are nearly same when the adsorption coefficient is 1.) Such an observation demands the movement of the organic substrates in the micro-valleys existing in the micropores. If the size of the organic molecule is larger than the diameter of the micropores then the chemisorption will occur very insignificantly. However, such a study with varying size of the organic molecule was not carried out extensively. The increased galvanostatic hydrogen arrest in the case of acid-chloride solution had been explained elsewhere[10] on the basis of the proton surface excess, Γ_{H^+}, on the plated electrodes. The present investigation automatically advances an alternate and simple explanation for the same.

Changing the medium from acid-sulphate to acid-chloride increases the surface area of the electrode by about 12%. To increase the surface area by 12% in acid-sulphate solution, we have to raise the temperature to about 100°. Hence the mere change over of the medium from acid-sulphate to that of acid-chloride in itself is equivalent* to increasing the temperature to about 100°C.

We have observed in the case of hydrogen adsorption on Pt/Pt electrode that an increase in the temperature increases the number of active sites. A similar behaviour exists with the chemisorption of organic compounds on Pt/Pt electrode as shown in Fig. 2. In the case of the anodic oxidation of chemisorbed residue formed from formaldehyde, the quantity, Q_M, increased from $4{\cdot}15\times10^{-2}$ to $5{\cdot}48\times10^{-2}$ coulomb as we increased the temperature from 4° to 80°. The ratio of the values of Q_M at 4° and 80° works out to 0·76. If we consider the ratio of the hydrogen regions at monolayer coverage, Q_{SH}, at 4° and 80° we get 0·74. Hence the hydrogen adsorption centres

*This equivalence corresponds to the enlargement in the hydrogen region alone. However, the complete effect of raising the temperature is not demonstrated, e.g. there is no decrease in the potential of the plateau of oxidation of chemisorbed species which we notice at high temperature.

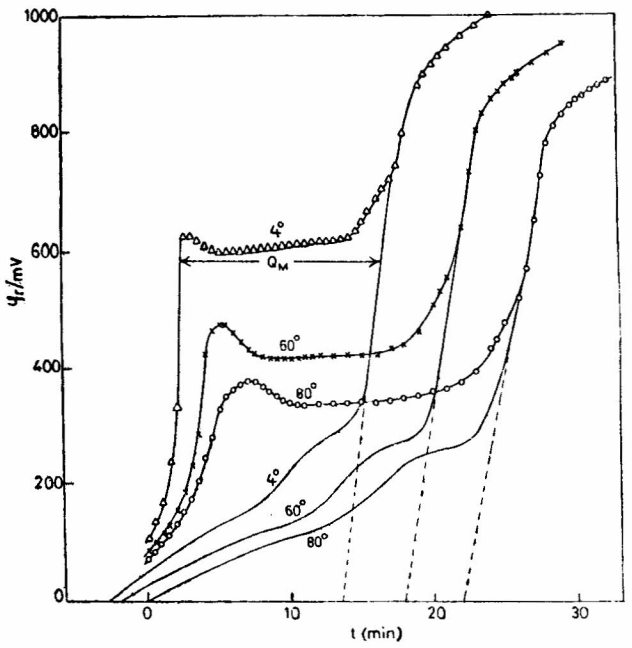

Fig. 2 — Anodic galvanostatic charging curves for the oxidation of chemisorbed formaldehyde on platinized-platinum electrode at 4°, 60° and 80° and in 0·5*M* H_2SO_4 at 1×10^{-4} amp/cm² (geom.)

and organic chemisorption centres are activated by temperature to the same extent. This is because of the fact that on the centres on which hydrogen adsorbs the organic adsorbates to chemisorb.

During our investigation with the chemisorbed intermediates we have noticed:

(i) Further, if we take an electrode and run the charging curves for the oxidation of the chemisorbed intermediates (formed from formaldehyde, methanol, formic acid, reduced carbon dioxide, etc.) at temperatures below or above the room temperatures, we obtain invariably the same oxidation potential plateaux. This observation is true for both very aged and moderately aged electrodes.

(ii) However, if we run the charging curves for the oxidation of the chemisorbed residues, we notice that the Q_M (organic coverage) is larger with fresh (and moderately aged) electrodes and the potential plateaux for their oxidation are also lower than that with extremely aged electrodes.

An explanation for the elevation of the potential plateaux of the oxidation of these residues observed with very aged electrodes can be advanced if we consider the significance of the Tafel plots. As we increase the current density, the potential plateau increases. In the case of very aged electrodes, the number of active sites are lesser and the true current passing per site is larger than in the case of moderately aged electrodes. Hence with very aged electrodes elevated potential plateaux is obtained.

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